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## Overcoming doping limits in MOVPE grown n-doped InP for plasmonic applications

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### ABSTRACT

Effect of the growth parameters on carrier concentration in MOVPE grown silicon-doped InP is studied. The dopant flow, V/III ratio and substrate temperature are optimized by considering the origin of the doping limits. In addition, two different group V precursors, namely PH<sub>3</sub> and TBP, are compared. The carrier concentration profile is measured using electrochemical capacitance-voltage (ECV) profilometry and the total concentration of silicon atoms is measured by secondary ion mass spectroscopy (SIMS) in order to evaluate the amount of Si atoms contributing as donors. The electron concentration about  $4 \times 10^{19} \text{ cm}^{-3}$  is achieved.

Optical properties of the samples are investigated by Fourier transform infrared reflection (FTIR) spectroscopy and are fitted by a Drude-Lorentz function.

### Introduction

Plasmonics has been an ever-growing subject of research in photonics during the past few decades. It has numerous applications ranging from subwavelength optical devices and spasers to chemical sensing. Traditionally, noble metals are considered as plasmonic materials in the visible and telecom (near-IR) ranges, with a plasma frequency being in the UV wavelength range. However, they are hardly applicable in the mid-IR, where they are too “perfect”. The quest for a suitable plasmonic material in near- and mid-IR, which is of special interest for sensing applications, is now open. One of the possible solutions is to involve semiconductors [1]. Optical and plasmonic properties of semiconductors are highly dependent on the carrier concentration. Therefore, highly doped semiconductors may exhibit plasmonic properties with acceptable losses in the near- and mid-IR ranges.

### Experimental details

Growth was carried out on S:InP wafers as the substrate, with a doping level between  $3.1 \times 10^{18}$  and  $8.4 \times 10^{18}$ , in a RDR-MOVPE system with hydrogen as the carrier gas. The total pressure of the growth chamber was 60 torr and trimethylindium (TMIn) and disilane were used as the precursors for In and Si respectively. Growth rate is found from [2]

$$A_1 p_{\text{TMIn}} + A_2 p_{\text{PH}_3/\text{TBP}}$$

in which  $p_{\text{TMIn}}$  and  $p_{\text{PH}_3/\text{TBP}}$  are the partial pressure of precursor gasses and  $A_1$  and  $A_2$  are constants which can be found experimentally from previous growth results. The partial pressures for the precursor gasses as well as their molar flows can be found from pertaining volume flows. Accordingly, five samples with a Si:InP epilayer thickness of 400 nm were grown with parameters given in Table 1.

ECV profilometry measurement was performed on the samples using pear etch (which is a mixture of HCl, HNO<sub>3</sub> and ethanol) as the electrolyte. The concentration of Si atoms in

three samples was measured using SIMS and compared to the ECV results in order to give a qualitative estimate to the portion of the atoms which are incorporated in doping.

FTIR reflection spectroscopy was performed on the samples in the wavelength range from 5  $\mu\text{m}$  to 37  $\mu\text{m}$  with the 12 degrees angle of incidence, and the dielectric function of InP with different doping levels was extracted from the results.

*Table 1: Growth parameters and the resulting doping levels for different samples*

Sample	P source	V/III molar ratio	Disilane flux/TMIn flux	Growth temperature ( $^{\circ}\text{C}$ )	Max. carrier concentration
1	$\text{PH}_3$	289.459	0.257	610	2.98 E19
2	$\text{PH}_3$	142.423	0.257	610	3.15 E19
3	TBP	25.61	0.257	610	3.24 E19
4	TBP	25.61	0.192	610	1.38 E19
5	TBP	25.61	0.257	515	2.5 E18
6	TBP	25.61	0.342	610	Rough surface

## Results and discussion

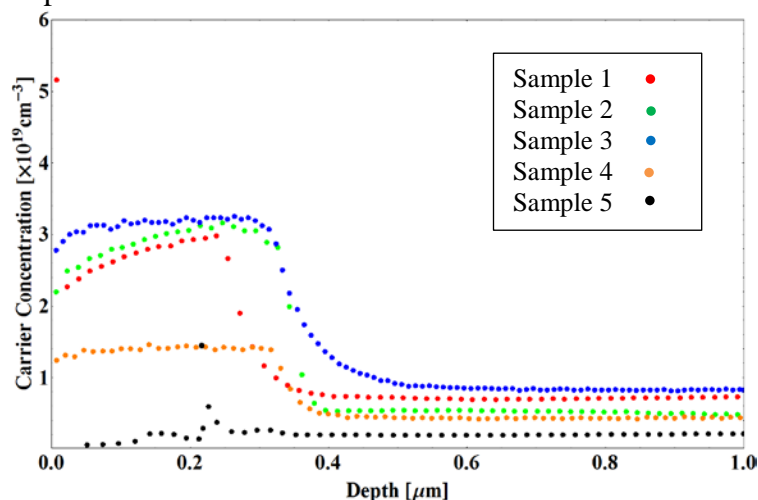
Figure 1 shows the carrier concentration profiles down to 1  $\mu\text{m}$  from the surface for all samples. The difference in the carrier concentration of the substrates is due to the uncertainty in the doping level of different wafers (3.1 - 8.4 E18).

Increasing V/III ratio is reported to increase the doping level up until a saturation point [3]. Since the growth rate is predominantly controlled by the group III element, by increasing V/III ratio more group III atoms will make bonds with Si atoms resulting in higher carrier concentrations. In our case, increasing V/III ratio resulted in slightly lower doping which might be interpreted in terms of saturation behaviour of this phenomenon.

Although allowable V/III ratio for TBP is much lower than that for  $\text{PH}_3$ , using TBP as the phosphorus precursor resulted in the higher doping concentration.

As it can be seen from the results, increasing the dopant precursor flux increases the carrier concentration up to the threshold point, above which Si clusters are formed on the surface making it rough. Figure 2 shows the DIC microscope image of the surface of sample 6 with precipitated Si clusters on it.

Growth temperature also plays an important role in the carrier concentration. Sample 5 which is grown in 515 $^{\circ}\text{C}$  has much lower carrier concentration due to low decomposition efficiency of the dopant precursor.



*FIG. 1: carrier concentration profile of the samples*

Figure 3 shows a qualitative comparison between SIMS and ECV results for samples 1 and 3. The concentration of Si atoms in both samples is much higher than the carrier concentration, which indicates that most of the introduced Si atoms do not contribute to doping, namely they are placed in wrong lattice positions making bonds with P atoms instead. This phenomenon which is known as self-compensation is one of the main sources which limits the maximum doping level in semiconductors [4].



FIG. 2: Precipitated Si clusters on the surface of sample 6 (DIC microscopy)

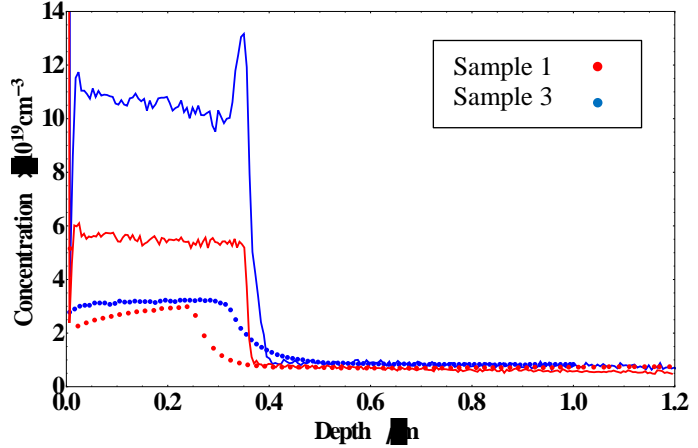


FIG. 3: SIMS results (solid lines) and ECV results (dots) for samples 1 and 3

The dielectric function of semiconductors in the IR range can be expressed in terms of a Drude-Lorentz function, in which the Drude term accounts for the free electrons plasma oscillations and the Lorentzian oscillators for different phonon absorptions [5]:

$$\varepsilon(\omega) = \varepsilon_{\infty} \left( 1 - \frac{\omega_p^2}{\omega^2 + i \omega \gamma} \right) + \sum_j \frac{S_j \omega_{f,j}^2}{\omega_{f,j}^2 - \omega^2 + i \omega \Gamma_j}$$

Here  $\varepsilon_{\infty}$ ,  $\omega_p$  and  $\gamma$  are the high-frequency dielectric constant, plasma frequency and electrons plasma damping respectively.  $S_j$ ,  $\omega_{f,j}$  and  $\Gamma_j$  are the strength, resonance frequency and damping for  $j$ th Lorentzian oscillator describing a phonon absorption on frequency  $\omega_{f,j}$ .  $\varepsilon_{\infty}$  is considered to be independent of the doping level.

FTIR reflection measurement was performed on samples 1-3 with a highly doped epilayer as well as bare InP substrates in the wavelength range between 5  $\mu\text{m}$  and 37  $\mu\text{m}$ . The intensity transfer matrix method, which eliminates interference fringes from the thick substrate layer [6], was used to calculate the reflection spectra of the samples. A curve fitting algorithm based on the Levenberg-Marquardt method was developed in order to fit the FTIR spectrometry results with the modelled reflection spectra and find the parameters of the Drude-Lorentz function. Figure 4 shows the reflection spectra from FTIR measurements together with the fitted curves for both semi-insulating and n-doped InP substrates. 13 Lorentzians were considered for the semi-insulating sample and 15 for the n-doped one in order to cover all the phonon absorptions in the spectra. After fixing the fitted parameters for the doped substrate, FTIR results for the samples with a highly doped epilayer were used to fit the Drude-Lorentz parameters of the epilayer. Table 2 shows the values of the fitted parameters.

## Conclusions

Effect of the MOVPE growth parameters on the carrier concentration in Si:InP is studied. Using TBP as the P precursor is found to result in higher carrier concentrations. Increasing the dopant flow rate increases the doping level up to a threshold, above which Si clusters are

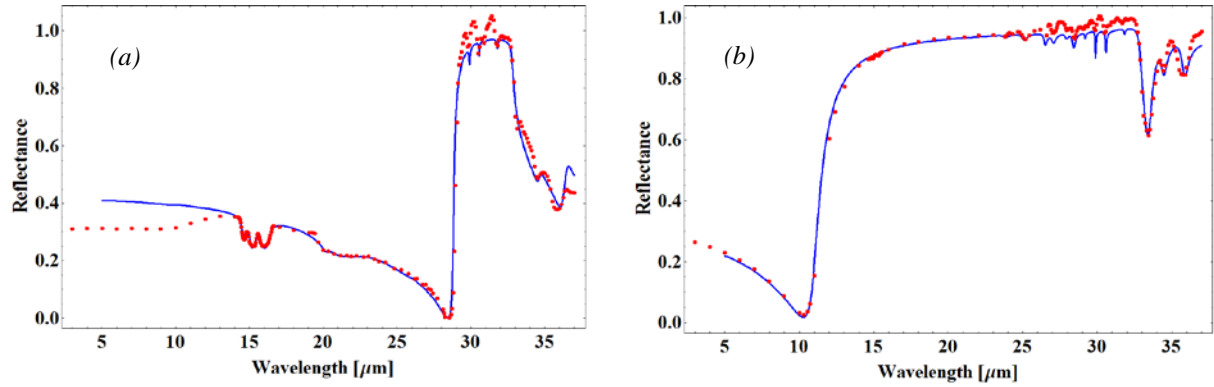


FIG. 4: FTIR reflection spectra (dots) together with the fitted curve (solid line), (a) semi-insulating substrate, (b) n-doped substrate

Table 2: Fitted Drude-Lorentz parameters (all frequency and damping units are  $\text{cm}^{-1}$ )

	$N\text{ (cm}^{-3}\text{)}$	$\omega_p$	$\gamma$		$j$																									
					1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20						
Semi-Insulating substrate	1.3 E7	0.0012	100.07	$S$	2E-4	0.001	0.001	3E-4	0.004	18E-4	0.001	15E-4	0.001	0.010	2.57	0.11	-													
				$\omega_f$	683.7	657.1	624.7	496.5	467.1	386	334.6	327.4	323.6	314.8	305.2	274.0														
				$\Gamma$	10.89	6	9.35	10	25	5.12	1	0.63	1	1	1.33	4.48														
n-doped substrate	6.5 E18	887.57	71.31	$S$	25E-4	34E-4	0.015	0.046	0.073	0.075	0.042	0.104	0.016	0.061	0.086	0.035	2.82	0.264	0.498	-										
				$\omega_f$	670.6	652.1	419.5	398.8	377.6	370.1	358.3	352.4	342.8	335.0	327.3	314.4	304.4	291.1	280.1											
				$\Gamma$	9.70	12.18	6	5.86	3.49	4.68	3.61	2.96	1	0.63	1	1.06	2.25	3.28	3.52											
Sample 1, epilayer	2.98 E19	1900.44	71.46	$S$	0.044	0.1	0.306	0.324	0.809	1.9	0.336	0.432	0.723	2.02	0.564	3.23	0.47	3.02	1.34	17.9	1.95	1.97	-							
				$\omega_f$	674.6	650.1	470.8	459.1	421.9	398.4	384.7	372.1	359.9	352.6	343	335.8	328.7	316.7	311.5	307	292	279								
				$\Gamma$	3.73	10.9	5.38	4.79	8.21	7.47	3.09	5.02	1.92	4.55	2.96	11.62	1.16	2.98	1.06	3.90	6.02	3.64								
Sample 2, epilayer	3.15 E19	1953.89	71.46	$S$	0.195	0.627	0.711	1.1	0.342	2.76	4.89	1.63	0.852	0.324	0.723	0.826	0.856	2.69	0.47	1.85	1.11	12.8	1.36	2.89						
				$\omega_f$	517	505	474.3	459.5	445.5	421.5	399.8	384.8	376.8	370.07	359.89	351.84	343	334.82	328.73	323.96	311.5	305.89	292.07	281.16						
				$\Gamma$	5.70	11.7	5.86	5.95	5.38	4.79	5.26	5.71	3.09	1.68	2.71	3.61	2.96	8.91	1.16	2.98	1.06	3.25	3.80	3.64						
Sample 3, epilayer	3.24 E19	1981.61	71.46	$S$	0.021	0.149	0.104	0.897	1.28	0.975	0.699	0.289	0.521	0.741	1.46	0.553	3.15	1.35	3.02	1.34	19.8	1.95	1.93	-						
				$\omega_f$	675	459.2	441.3	419	397.3	384.2	376.5	370.8	365.6	359.2	352.6	343	335.8	326.7	316.73	311.5	307	292	281.8							
				$\Gamma$	3	4.24	3.73	5.97	6.02	4.72	3.24	3.1	5.02	1.92	4.55	2.96	6.38	3.05	2.98	1.06	3.9	6.02	3.64							

formed on the surface of the samples. Lowering the growth temperature from 610°C to 515°C leads to a drastic decrease in the carrier concentration due to low cracking efficiency of the disilane precursor at low temperatures. Increasing V/III ratio makes a small decrease in the doping level in this case. Carrier concentration has a strong effect on optical properties of InP in the IR range. The plasma frequency of InP is highly dependent on the carrier concentration as it is predicted by the classical relations. In highly doped InP, effect of plasma resonance overshadows the effects of phonon absorptions in the mid-IR region and only very strong Lorentzian resonances remain effective in this case.

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